St. Joseph's Journal of Humanities and Science (Volume 4 Issue 1 January 2017) 47- 51

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St. Joseph's Journal of Humanities and Science
ISSN: 2347 - 5331

http://sjctnc.edu.in/6107-2/

CHARACTERIZATION OF NANOFIBER MAT PREPARED BY ELECTROSPINNING TECHNIQUE TO ACT AS AN INTERMEDIATE LAYER IN BPM

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Abstract

In recent years, electrospinning has garnered a lot of interest in the production of ultra fine continuous polymer fibers of varying diameters. The main goal of this study was to prepare a novel bipolar membrane using metal incorporated hydrophilic polymer nanofiber mat as an intermediate so as to investigate the effects of the hydrophilic interface on water splitting efficiency. The technique used for the nanofiber preparation is by electrospinning method and the polymer used for the nanofiber mat is Polyvinyl Pyrrollidone (PVP, a conducting polymer). The novelty in the work is incorporation of metal (Ti) into the nanofiber matrix during the electrospinning process itself for the enhancement of water splitting capacity. Thereby, the bonding of the metal with the nanofiber polymer matrix was stronger than obtained through any other process. This strength is directly focused towards the better efficiency in water treatment applications. The fabricated nanofiber mat was characterized using FTIR-ATR, SEM-EDAX and XRD techniques.

Keywords: Electrospinning; Polyvinyl Pyrrollidone; Ti metal incorporated nanofiber; Scanning electron microscope.

INTRODUCTION

Electrospinning is a broadly used electrostatic fiber fabrication technology which utilizes strong electrical forces to produce polymer fibers. Various diameters of fibers were produced ranging from 2 nm to several micrometers using more than 200 natural and/or synthetic polymer solutions[1]. The sub-micron range non-woven nanofibrous mats produced by this technique, offers various advantages like high surface area to volume ratio, tunable porosity and the ability to manipulate nanofiber composition in order to get desired properties and function. About 50 patents have been filed in the past 60 years[2] describing various experimental methodologies with different polymer melts and solutions. This has evinced more research interest and commercial attention due to its versatility and potential for applications in diverse fields[3-6].

Bipolar membranes (BPM) usually consist of anion and cation exchange layers. Upon strong electric field, all the ionic components are removed from the BPM and then water splitting occurs at the interface resulting in protons and hydroxyl ions. Hence, therefore the BPM performance significantly depends on the interface characteristics. Usually electric field enhanced water dissociation and catalytic proton transfer reaction are employed to explain the water splitting mechanism. In this sense, many researchers have tried to enhance the

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water splitting efficiency by modifying the interface properties[7-9]. From the literature, it was observed that introduction of either hydrophilic substance or metallic compounds as a water splitting catalyst at the interface considerably reduces the water splitting voltage due to increased wetness thereby promoting water dissociation reaction in a BPM interface[10].

The present work reports on the successful preparation of electrospun Ti metal incorporated Polyvinyl Pyrrollidone (PVP) nanofiber from its aqueous solution form. To the best of our knowledge, electrospinning of PVP from its aqueous solution have not been reported. It was expected that the enhanced hydrophilicity at the BPM interface accelerates the water splitting reaction because the hydrophilic polymer (PVP) increases the water activity by attracting water from the ion exchange layers to the space charge region. The other reason for choosing this polymer system was that conducting polymers like PVP with porous structure and high surface area are often considered to be useful as supporting materials for the incorporation of dispersed metal catalysts and development of high performance electro catalytic materials[11]. The Ti metal species immobilized in the PVP system improved the water splitting efficiency via metal catalytic reaction by increasing membrane wetness and enhancing the membrane conductivity. The prepared nanofiber mat was subjected to characterizations like FTIR-ATR, XRD and SEM-EDAX studies to identify the presence of structural groups and to study the morphology respectively.

EXPERIMENTAL METHODS

Materials

Conducting polymer Polyvinyl Pyrrollidone (PVP) (M.Wt: 14, 00,000) was procured from Sigma-Aldrich. Acetic acid and Ethanol was purchased from Merck and Titanium tetra-isopropoxide was obtained from Spectrochem, India.

Synthesis of Nanofiber Mat Using Electrospinning Process

The electrospinning process is based on the principle that strong electrical repulsive force overcomes weaker surface tension of a polymer solution at certain threshold to eject a liquid jet[13]. The typical set up of electrospinning apparatus used for the synthesis of nanofiber mat is shown in figure 4. Among polymers, synthetic polymers offer many advantages over natural polymers in terms of material properties. Depending on the type of solvent used, the intermolecular interaction in a polymer–solvent system can be either attractive or repulsive which affects its spin ability nature. In this work, the conducting polymer PVP of high molecular weight was dissolved in acetic acid and ethanol solvent mixture in the appropriate ratio before electrospinning and when it completely dissolves, forms polymer solution. Then titanium tetra-isopropoxide solution was added to this polymer solution and allowed to stir for 15 minutes. Then finally obtained polymer fluid was loaded in to the 2 ml syringes (3 No's) for multiple jet electrospinning. Thus, required quality of nanofiber mat was obtained using this process.

Effects of Various Parameters on Electrospinning

The electrospinning process is solely governed by many parameters[1]. The most significant parameters are high molecular weight, optimum concentration and high viscosity. Hence, the optimum conditions are obtained to finally result in the formation of more uniform fiber with large diameter. In case of very low molecular weight solution with low viscosity, bead formation is observed due to discontinuous fiber formation. Reducing the surface tension of a nanofiber solution resulted in fiber at lower electric field without beads.

Authors[1, 14-16] have reported that an increase in the applied voltage increases the electrostatic repulsive force on the fluid jet which ultimately favors the narrowing of fiber diameter. Though the syringe was linked to a high-voltage power supply (maximum up to 50kV), in the present work only 20kV electric voltage was used. The jet velocity and the material transfer rate mainly depend on the flow rate of the polymer solution from the syringe. A lower flow rate is more desirable as the solvent will get enough time for evaporation prior to reaching the aluminium foil on a rotating drum which act as a collector. Unavailability of proper drying time (i.e., high flow rate) may result in beaded fibers. In this present work the flow rate through the syringe pump was regulated using the PICO Espin 2.0 version software and was adjusted to 0.2ml/h for nanofiber mat. The fiber alignment is determined by the type of the target/collector and its rotation speed. Here collecting drum was regulated to rotate with a speed of 200 rpm, for getting aligned electrospun fibers more or less parallel to each other. The optimum distance between the tip of the syringe and collector was chosen to be 12-15cm (min. distance). High humidity during process resulted in circular pores on the fibers and increase in temperature results in decrease in fiber diameter.

Characterization Studies

The PVP-Ti nanofiber mat was subjected to FTIR-ATR analysis using Alpha T Bruker Optics FTIR spectrophotometer. The frequency of the sample was recorded at a resolution within the scanning range of 4000–500 cm^{-1} to confirm its nature and structural properties of the polymer. The morphology and the incorporation of metal in the nanofiber mat were observed using HITACHI S-3400 model SEM-EDAX. The surface of the materials was sputter-coated with gold before being subjected to SEM in order to make them electro-conductive. The phase analysis and crystallinity of the PVP and PVP-Ti fiber mat was analyzed by XRD using an X'Pert Pro diffractometer. The dried samples were mounted on an aluminium sample holder with scanning angle ranged from 1° to 80° and a scanning rate of 2° per min.

RESULTS AND DISCUSSION

FTIR-ATR analysis

The FTIR spectra of electrospun Ti incorporated PVP nanofiber mat is shown in figure 8.1. The appearance of peaks at 1430 cm-1 and 1742 cm-1 in the spectrum confirmed the presence of cyclic ring structure and the nature of the ring would be possibly 5-membered in the system respectively, whereas the peak at 1282 cm-1 confirms the stretching vibration of aryl –C-N group. The strong absorption peak at 1642 cm-1 infers the presence of carbonyl stretching in ketones. The weak and broad peaks arouund 3392 cm-1 was mainly due to the intramolecular H-bonding with C=O group. The vibration peaks due to symmetric stretching (vs) of C-H group in cyclic ring appeared at 2922 cm-1. The weak vibration bands in the region from 800-1200 cm-1 was due to the C-C stretching vibration of cyclic alkanes. The peak at region < 800 cm-1 was due to the alkanes C-H out-of-plane bending vibration. The weak band at 561 cm-1 was due to out-of-plane bending vibration and it confirms the presence of –N-R bonding in the system.

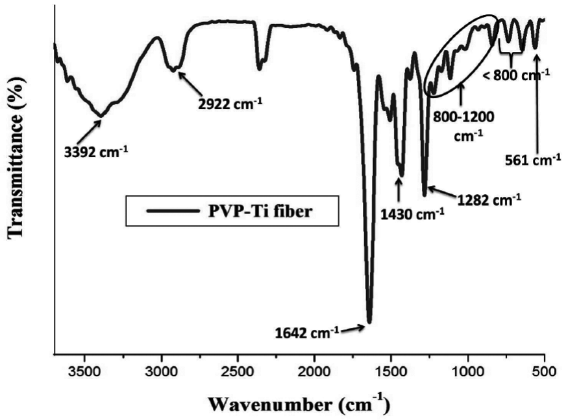


Figure 8.1 : FTIR spectra of electrospun PVP-Ti

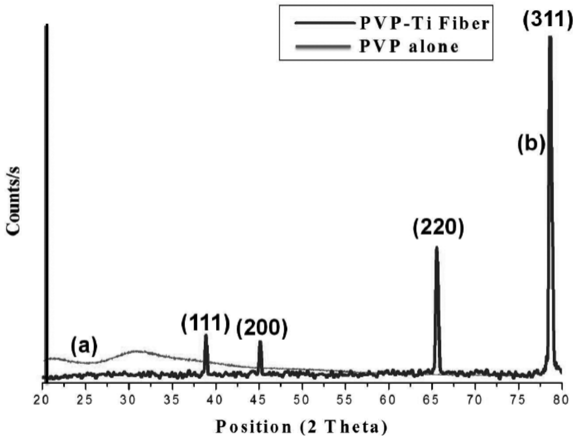


Figure 8.2 : XRD pattern for (a) PVP alone nanofiber mat.and (b) electrospun PVP-Ti nanofiber mat.

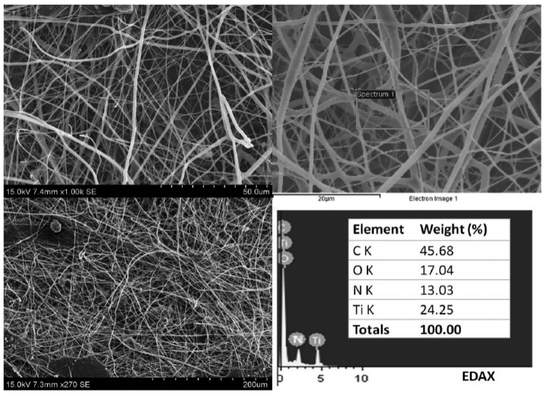
XRD analysis

The XRD patterns of electrospun Ti incorporated PVP nanofiber mat and PVP polymer alone are shown in figure 8.2. Since PVP polymer was semi-crystalline in nature the XRD pattern of it (a) shows a less intense and broad peak at value 2θ = 32° due to thermal motion within the crystallinities. Whereas in the case of (b) electrospun PVP-Ti nanofiber mat additionally 4 sharp and more intense peaks were observed, all of which confirms the presence of Ti metal in the fiber mat which was evidenced from the literature[12]. From the XRD pattern of fiber mat (b), it was inferred that a peak at 38.84° 2θ value corresponds to (111) plane; a peak at

45.11° 2θ value corresponds to (200) plane; an intense peak at 65.66° 2θ value corresponds to (220) plane and finally a highly intense peak at 78.59° 2θ value corresponds to more stable (311) plane of Ti and its high X-ray counts per seconds indicate occupation of higher number of atoms. These results were analogous to the XRD patterns of face centered cubic lattice system of pure Ti powder sample observed from the literature (JCPDS ICSD No. 041503 bearing PDF No. 88-2321). The crystallinity was due to the presence of different planes in the fiber mat. The count per seconds was found to be higher for (311) plane where more number of atoms has been occupied and then for (220) followed by (111) and finally for (200) plane.

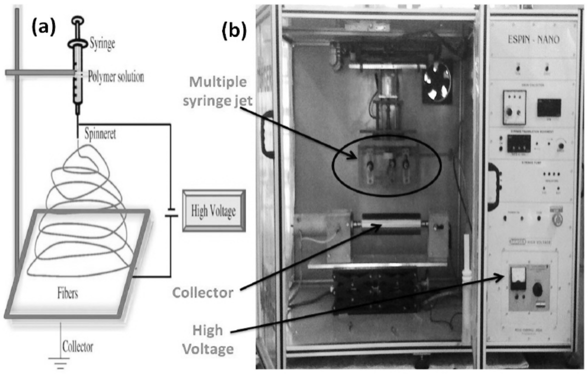
SEM-EDAX analysis

The surface morphology and elemental analysis of the electrospun PVP-Ti nanofiber mat were evaluated using SEM and EDAX instrument and the micrographs are shown in the figure 8.3. The SEM micrographs of nanofiber mat showed a long, continuous and good fiber mat formation without the formation of beads. The nanofiber mat has been made up of PVP and Ti metal which was evident from the obtained elements in the EDAX analysis.



Element	Weight (%)
C K	45.68
O K	17.04
N K	13.03
Ti K	24.25
Totals	**100.00**

Figure 8.3. SEM-EDAX Micrographs of PVP-Ti



(a) Schematic representation of Single jet mode electrospinning apparatus
(b) Multiple jet mode electrospinning apparatus.

Figure 8.4 : Different modes of electrospinning nanofiber mat. set up

CONCLUSION

Since electrospun nanofibers possess higher surface area to volume ratio than conventional fabrics, it could represent a next generation platform for the fabrication of fiber reinforced systems with enhanced performance. Moreover, nanofiber reinforced systems may significantly increase the interaction between the fibers and the matrix material, leading to better reinforcement than conventional fibers. In this paper we have reported the successful preparation of electrospun Ti metal incorporated Polyvinyl Pyrrollidone (PVP) nanofiber from its aqueous solution form. The prepared nanofiber mat was subjected to characterizations like FTIR-ATR, XRD and SEM-EDAX studies to determine the nature of a structural group present, phase analysis and morphology analysis of the fiber mat respectively.

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